ROUTINE DETERMINATION OF PER- AND POLYFLUORONATED ALKYL SUBSTANCES (PFAS) IN DRINKING WATER BY DIRECT INJECTION USING UPLC-MS/MS TO MEET THE EU DRINKING WATER DIRECTIVE 2020/2184 REQUIREMENTS

Hannah Willmer, Kari L. Organtini, Stuart Adams
Waters Corporation

Waters
THE SCIENCE OF WHAT'S POSSIBLE.™

INTRODUCTION

The EU has now regulated a set of 20 PFAS compounds in the updated European Drinking Water Directive 2020/2184. This acknowledges the high contamination potential of PFAS compounds and imposes a limit of 0.1 µg/L for the sum of 20 specified individual PFAS compounds that are considered a concern in water intended for human consumption.

Because of the widespread use of PFAS, required detection limits are in the low ng/L range and specific challenges must be addressed for sample collection, preparation, and analysis. Direct methods of analysis are limited and often require the use of SPE to reach lower limits of detection by purification and concentration. This creates challenges for sensitivity and chromatography especially when higher injection volumes are required, and contamination is difficult to avoid.

METHOD

Sample preparation, extraction and analysis:

Water was collected from sources of known soft and hard water areas in the UK and stored in 50 mL centrifuge tubes, mineral water was purchased from a UK retail outlet and stored in its original container. All samples were stored at room temperature.

A calibration range of 1 to 200 ng/L (0.6 to 120 ng/L in vial concentration) was used for all analytes. Quantification of spiked samples fortified at 2, 10 and 100 ng/L was calculated by matrix matched bracketed calibration prepared in respective blank matrix extract.

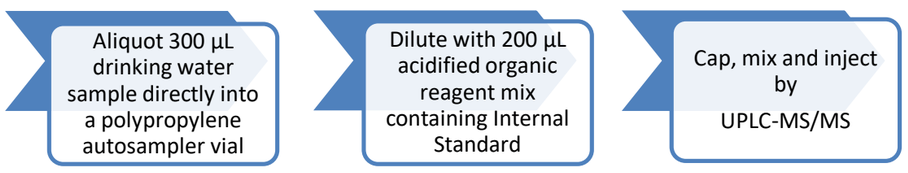


Figure 1. Sample preparation workflow

Effect of sample composition on peak shape: a careful balance is required for maximum performance when analyzing short and long chain PFAS compounds simultaneously. When diluting to a higher final organic content, a significant increase in sensitivity was observed for the less water-soluble longer chain PFAS but shorter chain PFAS peak shape started to deteriorate.
The final optimised ratio of sample composition was equivalent to:
60:29.9:10:0.1 v/v/v/v aqueous sample:acetonitrile:methanol:formic acid

Contamination from the chromatographic system and solvents can be unavoidable. Therefore, steps should be taken to minimize these contributions. An easily installed PFAS kit replaces items such as the conventional Teflon coated solvent lines with PFAS-free PEEK components. Additionally, installing an isolator column and extension coil helps delay residual background interferences in the mobile phase from co-eluting with the analytical peak from the injected sample.

Instrumental conditions:

UPLC System:	ACQUITY UPLC I-Class PLUS with fixed loop, fitted with Waters PFAS kit (p/n 205000588) and isolator column (p/n 186004476)
Column:	ACQUITY Premier BEH Shield RP18, 1.7 µm; 2.1 x 100 mm (p/n 186009498)
Mobile Phase A:	2 mM ammonium acetate in H2O:MeOH 95:5 (v/v)
Mobile Phase B:	2 mM ammonium acetate in MeOH
Column Temp:	45˚C
Injection Volume:	50 µL

MS System:	Xevo TQ-XS
Ionisation Mode:	US-
Acquisition:	MRM
Capillary Voltage:	1.00 kV
Cone Gas Flow:	150 L/hr
Desolvation Temp:	400˚C
Desolvation Gas Flow:	900 L/Hr
Source Temp:	110˚C

Full MRM parameters detailed in application note #720007413 at www.waters.com

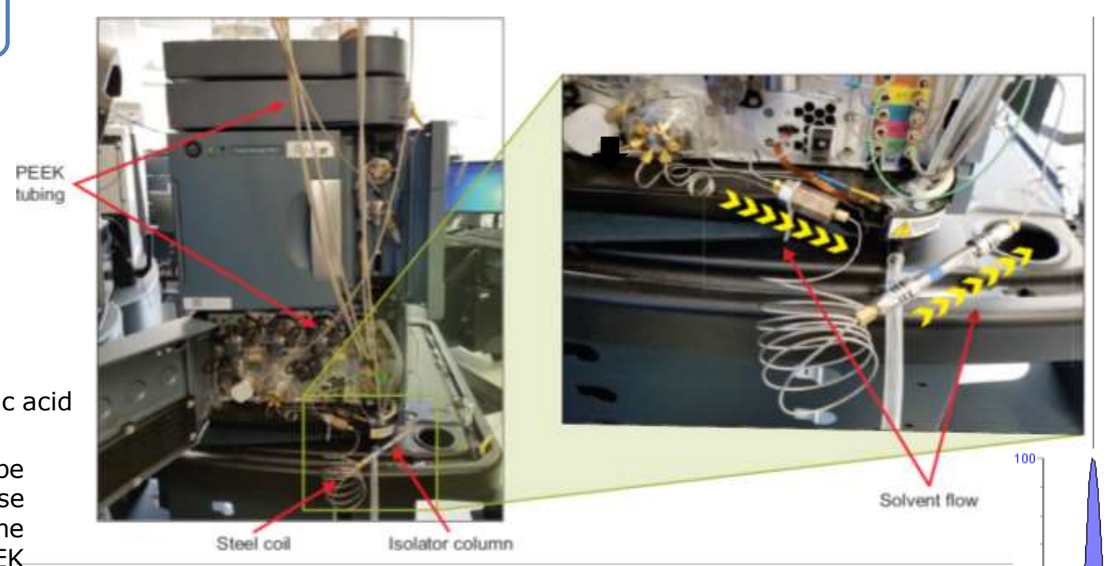
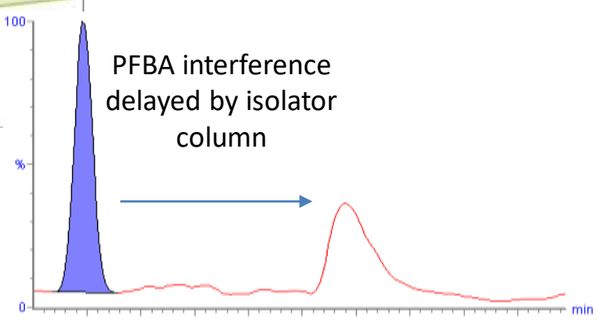
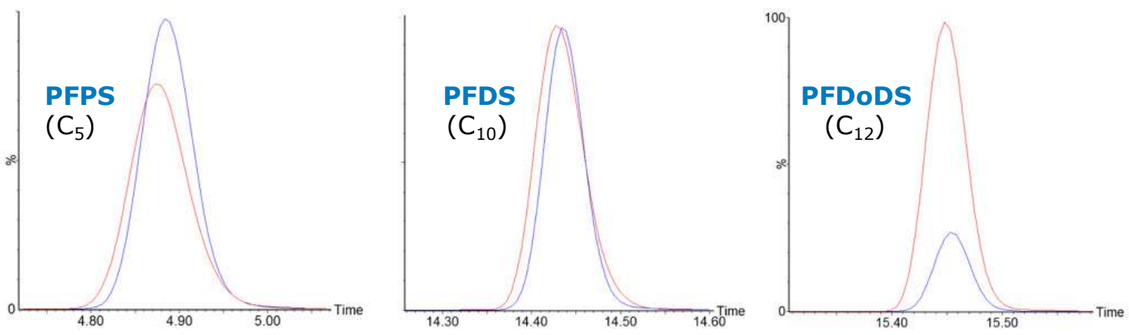


Figure 2. Use of PFAS kit to minimise and delay interference from system and mobile phases.



RESULTS AND DISCUSSION

Figure 3. Peak response of PFAS compounds comparing ACQUITY Premier (red) and ACQUITY UPLC (blue) column performance over a range of chain lengths. Demonstrated at 10 ng/L in LCMS grade water.

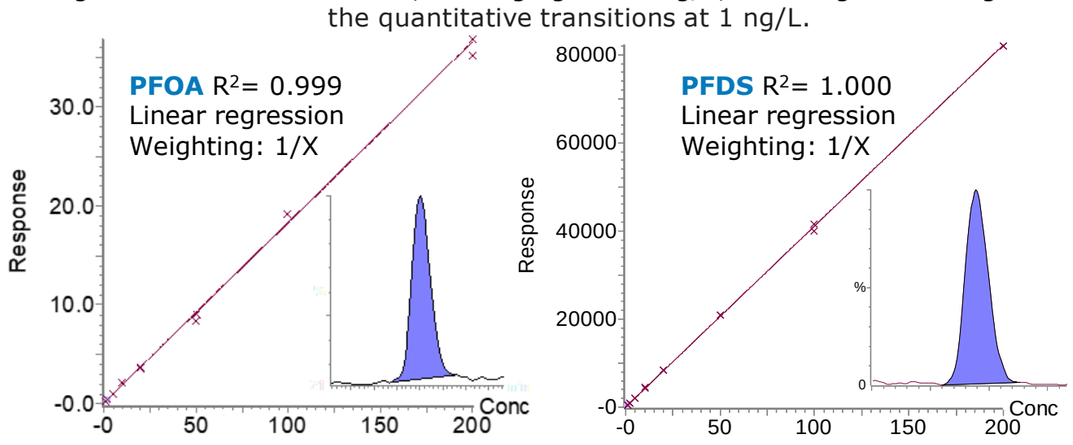


Advantages of using ACQUITY Premier Columns for longer chain PFAS: Longer chain PFAS (≥C10) displayed a significant gain in sensitivity using the ACQUITY Premier Column compared to the ACQUITY UPLC Column; up to 20 times the area and signal to noise at the longest chain length PFAS analysed, PFTrDS. There was little to no significant reduction in performance for the short-to mid chain PFAS. Figure 3 shows the comparison of compounds from a variety of chain lengths.
As the longer chain PFAS were substantially challenging in terms of sensitivity in the final sample composition, the enhancements identified with the ACQUITY Premier BEH Shield RP18 Column demonstrated why this column was selected for this application.

Residuals for all analytes were within 20%. All compounds achieved linear regression using 1/X weighting with R^2 values ≥0.990. Figure 4 shows the calibration curves of PFOA and PFDS. Overall retention time for all analytes across the 3 method validation batches was within 3.2% RSD and demonstrated retention time stability over the study regardless of water type.

All independent PFAS compounds, levels and matrices gave an average recovery by compound between 80 and 120%. Repeatability of the method was assessed from the recovery samples and all PFAS had an RSD below 13% with the exception of the longest chain sulfonate, PFTrDS, in soft water at 23.5%.

Figure 4. Matrix matched calibration curves of short chain PFOA in hard water and long chain PFDS in soft water, all ranging 1-200 ng/L, including chromatograms for the quantitative transitions at 1 ng/L.



Improving detection and sensitivity through use of the UniSpray ion source: The UniSpray ion source displayed a consistent enhancement in sensitivity for all compounds, measured by comparing peak area, peak height, and signal to noise. An average increase of 18 times in peak area and 5 times in signal to noise ratio was observed.

By improving the detection sensitivity for longer chain PFAS, the injection volume could subsequently be reduced to improve chromatography in the earlier eluting short chain PFAS such as PFBA. A final injection volume of 50 µL was determined and provided adequate sensitivity with suitable peak shape.

CONCLUSIONS

- Sensitive analysis to determine residues at concentrations as low as 1 ng/L in drinking water without the need for lengthy clean-up or concentration steps.
- Offers sufficient chromatographic retention, selectivity, peak shape, and stability.
- Confidence in results by reducing and separating possible system and solvent contaminants with the utilization of the Waters PFAS kit and isolation column for LC modification.
- Provides a total solution using a direct injection, UPLC-MS/MS method suitable for the detection and quantification of all 20 PFAS with an LOQ of 1 ng/L per compound which significantly exceeds requirements in the 2020 EU Drinking Water Directive.

TO DOWNLOAD A COPY OF THIS POSTER, VISIT WWW.WATERS.COM/POSTERS